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Morphological Behavior of Sulfonated Styrene-Ethylene/Propylene-Styrene Triblock Copolymers

by Brian D. Mather, Frederick L. Beyer, and Timothy E. Long

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Morphological Behavior of Sulfonated Styrene-Ethylene/Propylene-Styrene Triblock Copolymers

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14. ABSTRACT

Sulfonated block copolymer ionomers possessing short (1K g/mol) styrene blocks and various rubber block lengths were synthesized via sequential anionic polymerization of styrene, isoprene, and styrene followed by hydrogenation and sulfonation. The ionomers were then characterized by small-angle x-ray scattering (SAXS) and atomic force microscopy (AFM). The SAXS data indicate the presence of microphase-separated sulfonated styrene domains within the rubber phase. The morphology of the phase separation in this system is not clear from SAXS due to the absence of higher order maxima. Increased Bragg spacing was observed as the rubber block molecular weights increased, but decreased upon neutralization of the sulfonic acid groups with sodium hydroxide. The intensity of the SAXS maxima increased for shorter rubber block segments. AFM images confirmed the presence of microphase-separated domains which appear spherical.

15. SUBJECT TERMS

block copolymer, SAXS, ionomer, sulfonated polystyrene, SEPS

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1. Introduction

Sulfonated block copolymers have drawn interest in recent years due to their applications in fuel cells (*1*), membranes (*2*), and elastomers (*3*). Sulfonated block copolymers exhibit morphological differences from their nonionic counterparts. The strength of the association of ionic groups in these materials increases the Flory-Huggins interaction parameter χ for phase separation. The increased drive for phase separation in these systems enables lower block molecular weights while maintaining phase separation due to the fact that the product χN, where N is the degree of polymerization, is the criterion for phase separation. Sulfonated styrene-ethylene/propylene-styrene triblock copolymers with short styrene end blocks (~1000 g/mol) and variable length ethylene/propylene (hydrogenated polyisoprene) rubber sequences are being studied in this project. The importance of the length of the rubber block on morphology and mechanical properties as a function of the critical molecular weight for entanglement is a specific focus of this work.

Small-angle x-ray scattering (SAXS) is critical to the investigation of morphology of traditional ionomers (such as Nafion), block copolymers, and block copolymer ionomers (*4–6*), providing evidence of morphological structure in microphase separated materials. SAXS has been used extensively to characterize the morphology of block copolymers due to Bragg diffraction maxima which identify characteristic microphase-separated morphologies in well-ordered samples. SAXS has also been used extensively to study ion-containing polymers. SAXS of ion-containing polymers usually shows a characteristic "ionomer peak" corresponding to a characteristic length scale of 2–6 nm, generally assigned to microphase-separated ionic clusters (*4, 7*).

2. Experimental

2.1 Materials

Styrene (99%) and isoprene (99%) monomers were purchased from Aldrich and purified by vacuum distillation from calcium hydride followed by distillation from dibutylmagnesium and storage under nitrogen at $-15\ ^{\circ}$C. Sec-butyllithium (12% in hexanes/heptane) was purchased from FMC Lithium Co. Dibutylmagnesium (1.0 M in heptane) and triethylaluminum (1.0 M in hexanes) were purchased from Aldrich and used as received. Nickel (II) 2-ethylhexanoate (8% in mineral spirits) was purchased from Shepherd Chemicals and used as received. Cyclohexane was purified by passage through molecular sieves and alumina under nitrogen. Anhydrous 1,2-dichloroethane was purchased from Aldrich and used as received. Citric acid was purchased from Aldrich.

2.2   Synthesis of Styrene-Isoprene-Styrene Triblock Copolymers

Polymerizations were conducted in a 600-mL glass reactor fitted with magnetic stirring, steam/cold water heating/cooling coils, a thermocouple, and temperature controller, as well as ports for introducing nitrogen, cyclohexane, monomers, and initiators and for draining and venting. The reactor was filled with 400 mL of dry cyclohexane under nitrogen and thermostated to 40 ^{o}C. Then 2.06 mL (18.1 mmol) of styrene was injected into the reactor followed by 1.60 mL of sec-butyllithium (2.0 mmol, 1.25 M in hexanes) and an orange color rapidly developed. The polymerization was allowed to proceed for 5 hr and samples were taken at intervals to ensure block formation was complete. Isoprene, 55 mL (550 mmol) was injected and the color immediately changed to light yellow. The polymerization was continued for 18.5 h and multiple samples were removed to ensure complete conversion. The final styrene aliquot (2.10 mL, 18.1 mmol) was injected finally and again polymerized for 5 hr. The polymer was then terminated with degassed methanol, precipitated in methanol, dried in vacuo at 50 ^{o}C, and stored in a freezer at –15 ^{o}C. SEC analysis revealed P(S-*b*-I-*b*-S) block molecular weights of 1.2K, 17.1K, and 0.5K respectively, with a molecular weight distribution (M_w/M_n) of 1.01.

2.3   Hydrogenation of Styrene-Isoprene-Styrene Triblock Copolymers

Hydrogenations were carried out in a similar reactor system as for the polymerizations. Nickel octoate/triethylaluminum hydrogenation catalyst was first prepared by adding triethylaluminum solution (4.8 mL, 4.8 mmol) to nickel 2-ethylhexanoate solution (5.7 mL, 1.34 mmol) in 20 mL dry cyclohexane dropwise with stirring under nitrogen. The catalyst solution was allowed to stir under nitrogen for 15 min prior to use. Then, 6.0 g of styrene-isoprene-polymer was dissolved in 100 mL dry cyclohexane under nitrogen and cannulated into the glass reactor fitted with magnetic stirrer and filled with 400 mL of cyclohexane. Finally, a few drops of catalyst solution were cannulated into the reactor and the reactor was pressurized to 90 psig with hydrogen gas and heated to 50 ^{o}C. Hydrogenation levels were monitored by sampling out, removing the catalyst with citric acid washes and obtaining ^{1}H NMR spectra. The hydrogenations were carried out to high conversion, >99%. The catalyst was removed by washing with citric acid solution (10 weight-percent) for 24–48 hr.

2.4   Sulfonation of Styrene-Ethylene/Propylene-Styrene Triblock Copolymers

Hydrogenated styrene-isoprene-styrene triblock copolymer (4.20 g) was charged to a 500-mL round-bottom flask and dissolved in 140 mL of cyclohexane and thermostated to 50 ^{o}C. Acetyl sulfate (25 equivalents relative to styrene) was generated separately through the addition of sulfuric acid (10.1 g, 101 mmol) to acetic anhydride (16.6 g, 163 mmol) in 1,2-dichloroethane (100 mL) at 0 ^{o}C. After stirring vigorously, the acetyl sulfate was added to the polymer solution dropwise through an addition funnel. The sulfonation reaction proceeded for 24 hr. The polymer was isolated by dripping the crude product into boiling water, removing the solvent by flashing. Water was repeatedly exchanged to completely remove the acetic and sulfuric acid

impurities. The polymer was then dissolved in tetrahydrofuran and dialyzed against deionized water to further remove acidic impurities. Final isolation involved rotary evaporation of the aqueous suspension followed by vacuum drying.

2.5   Titration and Neutralization of Sulfonated Styrene-Ethylene/Propylene-Styrene (SEPS)

Sulfonated SEPS block copolymer (0.116 g) was dissolved in tetrahydrofuran (30 mL) and titrated with standardized 0.023 M NaOH (aq) (0.75 mL) using thymol blue as an indicator. The degree of sulfonation (62%, relative to styrene content) was determined from the average of three titrations. Then, neutralization of a larger portion of polymer (3.89 g) was performed by addition of 45.1 mL (1 equiv) of 0.023 M NaOH. The neutralized polymer was then isolated by rotary evaporation of the solvent mixture and vacuum drying of the polymer.

2.6   Small-Angle X-ray Scattering (SAXS) Measurements

Block copolymer samples in the sulfonic acid form were dissolved in THF and cast in Teflon molds. Sodium-sulfonated block copolymers were dissolved in toluene/methanol (95/5 w/w) and cast in Teflon molds. The films were dried in a vacuum oven at room temperature for 4 days and stored at -15 $^{\circ}$C until use. SAXS data were collected on the U.S. Army Research Laboratory (ARL) SAXS instrument, located at Aberdeen Proving Ground, MD. $Cu_{K\alpha}$ X-ray radiation was generated using a Rigaku Ultrax18 rotating anode x-ray generator operated at 40 kV and 115 mA. A Ni foil was used to filter out all radiation except the $Cu_{K\alpha}$ doublet, with an average wavelength, λ, of 1.542 Å. The ARL instrument uses a Molecular Metrology camera with 300-, 200-, and 600-μm pinholes for x-ray collimation. Two-dimensional (2-D) data sets were collected using a Molecular Metrology 2-D multi-wire area detector located ~1.5 m from the sample. After azimuthal averaging, the raw data were corrected for detector noise, absorption, and background noise. The data were then placed on an absolute scale using a glassy carbon sample 1.07 mm thick, previously calibrated at the Advanced Photon Source of the Argonne National Laboratory as a secondary standard. The one-dimensional intensity data are given as a function of the magnitude of the reciprocal scattering vector, q, where $q = 4\pi\cdot\sin(\theta)/\lambda$, and 2θ is the scattering angle. All data reduction and analysis were performed using Wavemetrics Igor Pro v. 5.04.

2.7   Atomic Force Microscopy (AFM) Measurements

A Veeco Dimension 3000 scanning probe microscope with a Nanoscope IIIa controller was used for tapping-mode AFM. Sulfonated polymers spin coated onto silicon wafers and dried under vacuum were imaged at a set-point ratio of 0.6 at magnifications of 1 μm $\times$ 1 μm. Veeco's TAP 150 tips having a spring constant of 2.5–10 N/m were utilized for imaging.

2.8 Size Exclusion Chromatography and Differential Scanning Calorimetry

Size-Exclusion Chromatography (SEC) was performed at 40 °C in HPLC-grade tetrahydrofuran at a flow rate of 1 mL/min using a Waters size-exclusion chromatographer equipped with an autosampler, 3 in-line 5 μm PLgel MIXED-C columns. Detectors included a Waters 410 differential refractive index (DRI) detector operating at 880 nm, and a Wyatt Technologies miniDAWN multiangle laser light scattering (MALLS) detector operating at 690 nm, which was calibrated with polystyrene standards. The refractive index increment (*dn/dc*) was calculated online. All molecular weight values reported are absolute molecular weights obtained using the MALLS detector. Differential Scanning Calorimetry (DSC) was performed on a Perkin Elmer Pyris 1 instrument under a nitrogen flush at a heating rate of 10 ºC/min. ^{1}H NMR spectroscopic data was collected in CDCl$_3$ on a Varian 400 MHz spectrometer at ambient temperature.

3. Results and Discussion

3.1 Polymer Synthesis

Styrene-isoprene-styrene triblock copolymers were synthesized through sequential monomer addition (figure 1). Anionic polymerization techniques allowed control of molecular weight and the synthesis of well-defined block copolymers for subsequent fundamental studies. Narrow molecular weight distributions are critical for establishing known block molecular weights, especially for the synthesis of short (1000 g/mol) endblocks. SEC analysis during the polymerization demonstrated complete conversion of each block in the time intervals chosen, which established the absence of tapering between the blocks. Furthermore, the SEC showed complete crossover between blocks and the absence of dead chains. The final block copolymer molecular weights are tabulated in table 1. Typical polydispersities are greater than 1.02. Hydrogenation of the block copolymers was achieved using a conventional nickel/aluminum catalyst which selectively hydrogenated the isoprene blocks. Hydrogenation was important due to the reactivity of olefin groups towards sulfonating reagents. Sulfonation was accomplished using acetyl sulfate, which has been recognized as a mild sulfonating agent. Sulfonation was conducted in a mixture of cyclohexane and dichloroethane (~50:50) due to the poor solubility of the precursor block copolymers in pure dichloroethane. Although an excess sulfonating agent was used, the sulfonation of hydrogenated diene-containing block copolymers typically reached a maximum conversion near 50–60%, which is likely due to micelle formation during the reaction in cyclohexane/dichloroethane; turbidity ensued as sulfonation occurred in the course of the reaction.
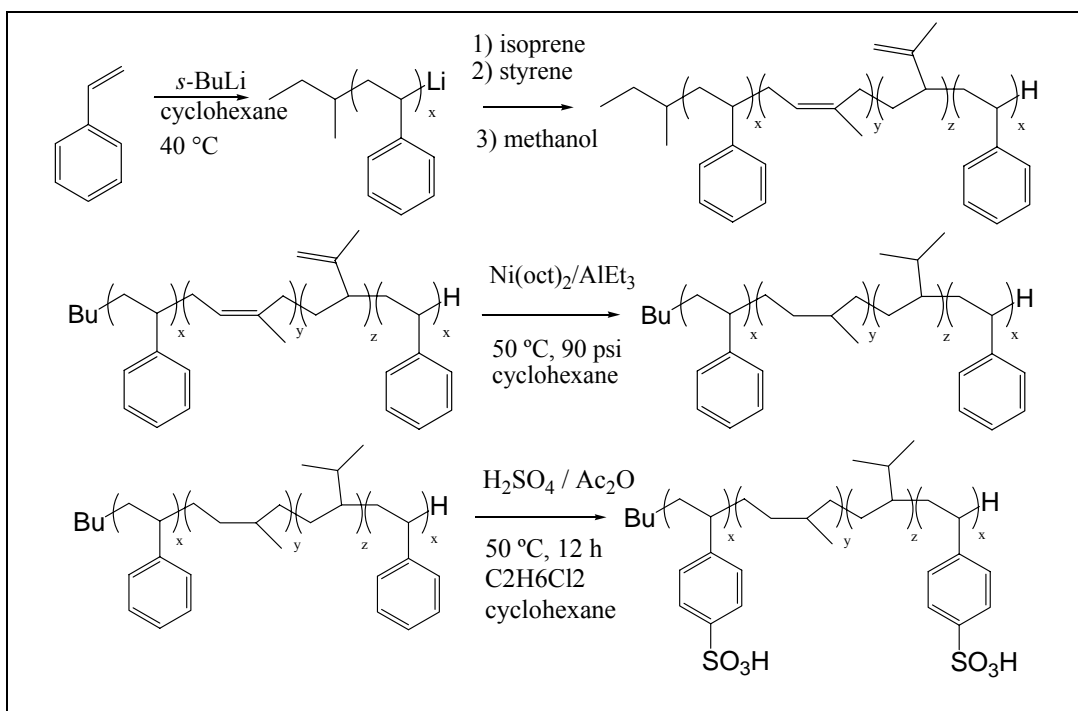
Figure 1. Synthesis of sulfonated block copolymers via sequential addition anionic polymerization.

Table 1. Compositional analysis of block copolymers.

Sample	Calculated SEPS Block Molecular Weights	M_w/M_n	Percent Styrene Content[a] (weight-percent)	Percent Hydrogenation[b] (mol/percent)	Percent Sulfonation[c] (mol/percent styrene)c	SEPS T_g [d] (ºC)
65A	1.0K, −10.0K, −0.4K	1.01	12.2	99.4	45	−54
114	1.2K, −17.1K, −0.5K	1.01	9.1	99.8	62	−57
65C	1.0K, −27.5K, −0.8K	1.02	6.1	98.7	46	−56

[a] SEC analysis, calculated from block molecular weights adjusted for hydrogenation.
[b] ^{1}H NMR analysis.
[c] Titration against 0.02 M NaOH$_{(aq)}$ in tetrahydrofuran.
[d] DSC, 10 ºC/min, N$_2$.

3.2 SAXS Characterization

SAXS is a powerful tool for the analysis of microphase separated systems. It provides insight into the morphology of samples and probes the bulk properties of samples in contrast to microscopy techniques. Those methods, such as AFM, examine only minute portions of the sample bulk or surface and may produce information which differs from the structure of the sample overall. SAXS is sensitive to electron density fluctuations through a sample, making it a

useful tool for examining ionomers due to the presence of nanoscopic ionic aggregates in these materials. These aggregates are easily detected in the case of ionomers due to the presence of metal counter ions and other heavy atoms such as sulfur.

The unsulfonated precursor SEPS polymers produced a scattering maximum in only one case and had very low scattering intensities in general (figure 2). The low volume fraction of styrene and the low degree of polymerization (DP) of the styrene blocks in the unsulfonated precursor materials would be expected to result in a homogeneous material. However, for the 65A precursor polymer, a weak and broad maximum is observed at $q^* = 0.058$ Å^{-1}, corresponding to $d = 10.8$ nm in real space, indicating that the volume fraction of styrene was large enough to cause microphase separation. The absence of a high-temperature ($\sim$100 ^{o}C) glass transition in DSC measurements of these polymers along with the absence of significant scattering suggests phase mixing for most of these polymers. Upon sulfonation, the drive for phase separation increases as measured by an increase in the χ parameter. Furthermore, the volume fraction of the styrenic block increases due to the presence of sulfonic acid or sodium sulfonated functional groups. These changes lead to the development of microphase separated morphologies.
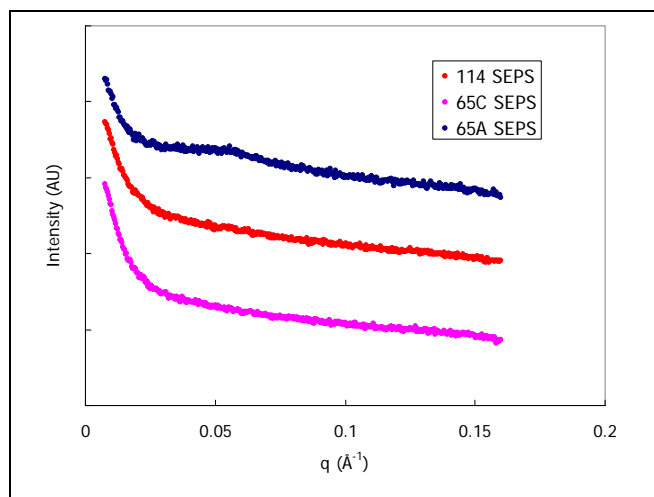
Figure 2. SAXS measurements of precursor SEPS polymers in between Kapton films. Intensities are not absolute due to background scattering from the Kapton film and are shifted vertically for clarity.

The SAXS experiments in this study clearly indicate the presence of microphase separation in the sulfonated styrene-ethylene/propylene-styrene block copolymers. All the samples showed a single peak in the one-dimensional scattering data (figure 3). The absence of higher-order peaks in the SAXS data reveals a lack of long-range ordering in these materials. The scattering maximum is believed to arise from scattering from the partially sulfonated polystyrene domains which are dispersed in the hydrocarbon ethylene/propylene matrix, akin to the scattering from disordered block copolymers or polyurethane materials.

Figure 3. Two-dimensional SAXS image (left) and 1-D SAXS profile (right) for the sulfonated SEPS (sample 65A) in sulfonic acid form.

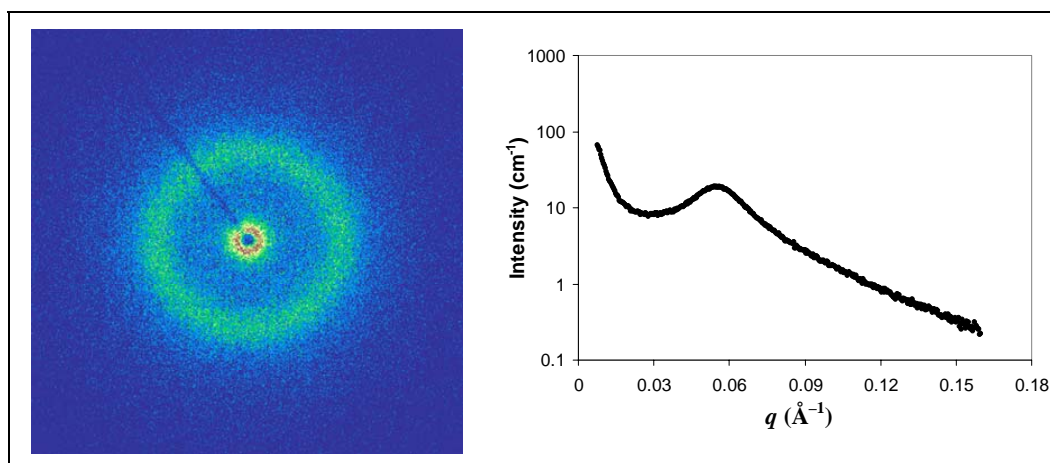Other researchers have observed a shift in morphology due to sulfonation, such as from cylindrical to lamellar morphologies (*4*), apparently due to the increased drive for microphase separation and the thermodynamic driving force to minimize interfacial surface area. Lu et al. have studied similar sulfonated styrene-ethylene/butylene-styrene polymers and have observed peaks in SAXS arising from both block copolymer microphase separation (d = 10–30 nm) as well as from ionic aggregation (d = 2–6 nm). They concluded that the ionic aggregates resided within the phase separated styrene domains (*7, 8*). Similar ionic peaks were also observed in Nafion[*] (*9*). An ionomer peak is not observed in the present studies. However, this may be due to the fact that films were prepared by solution casting which was shown to suppress the ionomer peak (*7*). Also, the high level of sulfonation was shown to shift q values above 0.2 Å^{-1} (for 18 mol% sulfonation), an angular range which was not examined in this experiment (*7*).

Comparisons among scattering profiles for polymers with differing rubber block molecular weights provides some insight into the progression of the morphology with molecular weight. Figure 4 shows that scattering maxima for the three polymer samples in the sulfonic acid (SO$_3$H) form. The intensities of the scattering maxima appear to increase with decreasing molecular weight. This is expected due to the increase of the sulfonated styrene volume fraction with decreasing rubber content. Since the sulfonated styrene domains are responsible for the scattering, an increase in the sulfonated styrene content should result in a stronger scattering signal, as observed.

Another variation among the sulfonated samples is in the position of the maxima. In the microphase separated morphology, the position of the scattering maximum yields the average spacing between domains, given in table 2. The peak positions were obtained by fitting the

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[*]Nafion is a registered trademark of E.I. duPont de Nemours Company, Wilmington, DE.
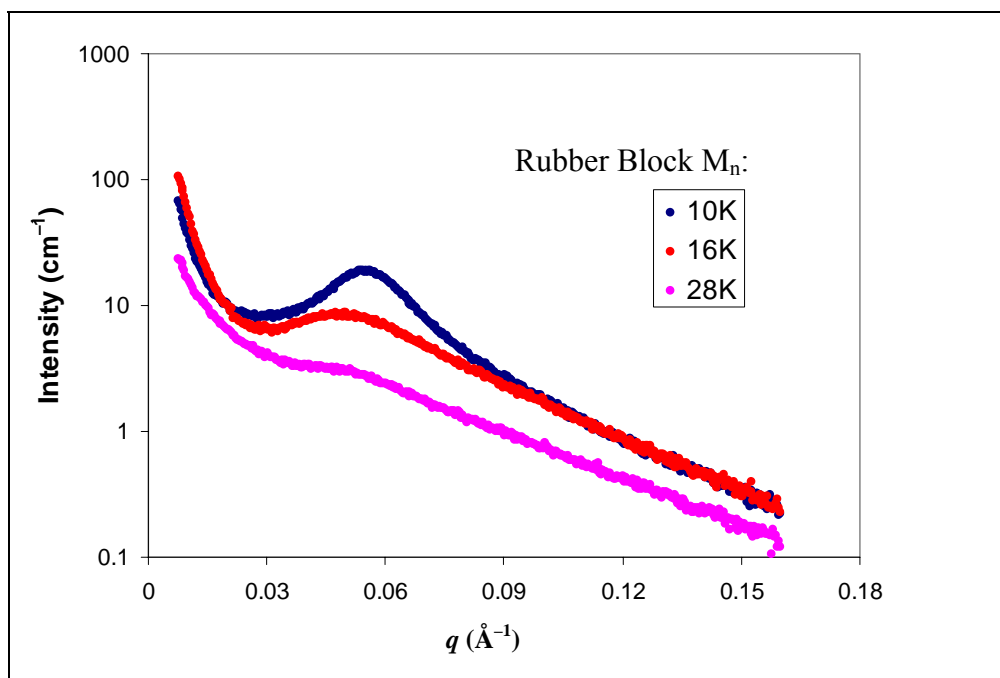
Figure 4. One-dimensional SAXS profiles for sulfonated block copolymers of varying rubber block molecular weights.

Table 2. Summary of scattering maxima position and Bragg spacing for sulfonated block copolymers.

Sample	Rubber Block M_n	Form	q^* (Å^{-1})	d (nm)
65A	10	SO_3H	0.055	11.4
—	10	SO_3Na	0.061	10.3
114	16	SO_3H	0.049	12.6
—	16	SO_3Na	0.053	11.9
65c	28	SO_3H	0.047	13.4
—	28	SO_3Na	0.049	12.9

scattering intensity with a Gaussian function and a linear background over a narrow range of q encompassing the peak. The interdomain distances calculated in this manner for the sulfonated block copolymers range from 10 to 14 nm, and appear to increase with increasing molecular weight. This trend is especially pronounced for the sulfonic acid series of block copolymers, which exhibited an 11.4-nm spacing for the 10-K rubber block (sample 65A), a 12.6-nm spacing for the 16-K rubber block (sample 114) and a 13.4-nm spacing for the 28-K rubber block (sample 65C). The increase in the distance between sulfonated styrene domains with increasing rubber block molecular weight was expected for these polymers, given that the spacing between the sulfonated domains on a molecular level is increasing. A similar trend is observed in the

sodium sulfonated form of the block copolymers. Sobry et al. observed a similar trend of interdomain spacing with molecular weight for telechelically functionalized ionomers, finding that the interdomain spacing was proportional to the root-mean-square end to end distance (*10*).

The SAXS spectra of the sodium-sulfonated polymers featured decreased Bragg spacings compared to the sulfonic acid polymers (table 2). This is characterized in the SAXS data as a shift in the scattering maxima to higher q upon neutralization of the polymer (figure 5). The smaller spacing between hard phases may arise from a "tightening" of the physical network structure due to the increased attractive forces between ionic groups when compared to neutral sulfonic acid groups. Lu et al. have observed a similar trend with oil-swollen sulfonated SEBS which was attributed to increasing strength of association (*8*). Another observation from Lu et al. is a broadening of the SAXS peak with increasing strength of association, with the breadth increasing in the order of "precursor" < "SO_3H" < "SO_3Na." Such broadening is clearly visible in comparing the sulfonic acid-containing polymers with the sodium-sulfonated ionomers (figure 5). The explanation provided was based on the stronger interactions in the sodium sulfonated polymers hindering the development of the morphology during solvent evaporation and concomitant film formation.
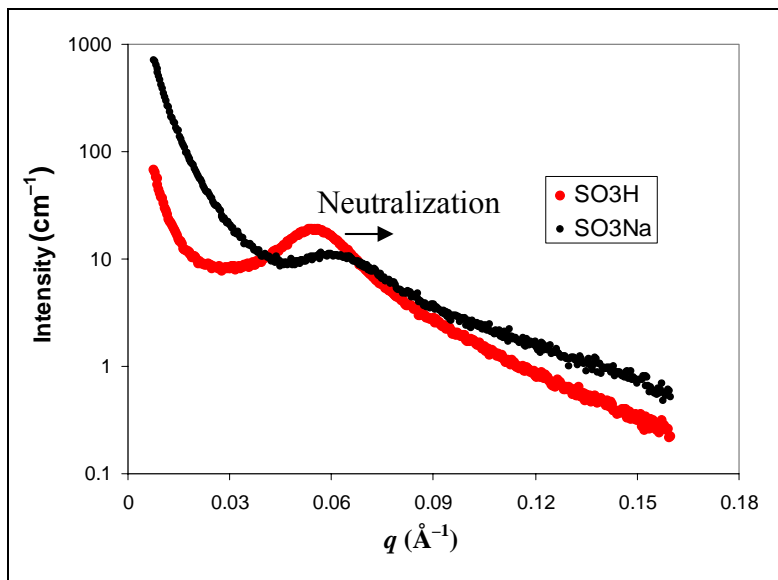
Figure 5. Effect of neutralization on the scattering maxima in the
sulfonated block copolymer (sample 65A).

3.3   AFM Characterization

Tapping mode AFM is a valuable tool for characterizing block copolymer surfaces. In particular, the phase image typically provides rich information if a hard and soft phase are both present. The phase image represents the phase lag between the cantilever tip response and the drive frequency. Figure 6 shows AFM characterization of sample 114 in sodium sulfonated form.

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Figure 6. AFM characterization of sample 114 in sodium sulfonated form, height image (left), phase image (right).

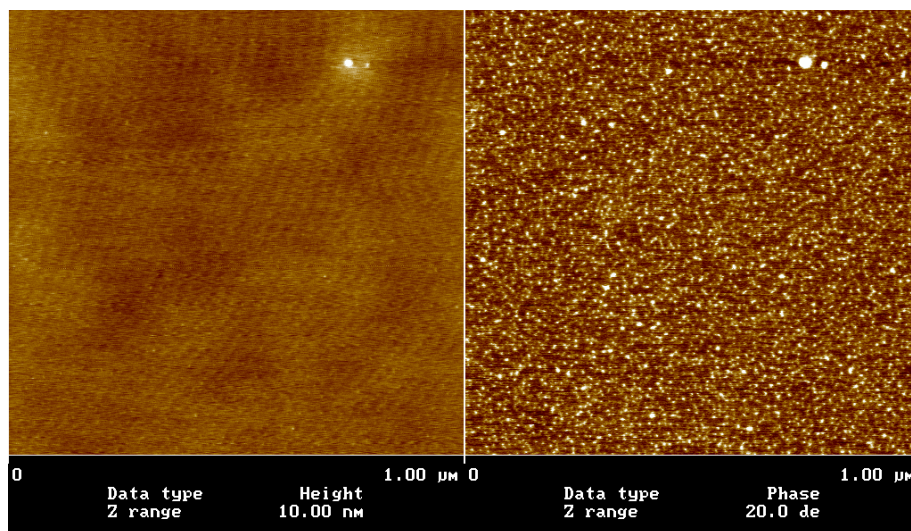AFM studies of the sulfonated block copolymers also revealed microphase separation at the surface, with harder sulfonated styrene domains dispersed in a soft hydrogenated diene matrix visible in the phase image. The smoothness of the topography images suggested that the structure present in the phase image did reflect "hard" and "soft" phases. The hard domains appeared to exhibit a spherical morphology as would be expected for the small styrene volume fractions. These domains are clearly not ordered in the material, corroborating the lack of higher-order peaks in the SAXS experiments. Similar images are obtained from spin-casting samples on silicon and imaging solvent-cast films, suggesting that the rate of evaporation is not preventing the ordering of the material. A cursory examination of the AFM images reveals hard domain spacings close to those obtained in SAXS experiments (~12–18 nm). AFM characterization of the unsulfonated precursor polymers also confirmed the absence of microphase separation.

4. Conclusions

Novel, short outer block sulfonated SEPS triblock copolymers were synthesized, then characterized via SAXS and AFM. The polymers exhibited microphase separation in which the minority component, sulfonated polystyrene forms a dispersed, hard phase in the soft, ethylene/propylene rubbery matrix. The sulfonated polystyrene phases appeared roughly spherical in shape, and no evidence of long-range order was observed. The interdomain spacing measured by SAXS allowed an analysis of the effects of the rubber block molecular weight and neutralization. Increasing rubber block molecular weight resulted in increased interdomain

spacing as well as lower scattering intensity. Neutralization of the block copolymers to the sodium sulfonate form resulted in a shift of the interdomain spacing to smaller values, suggesting a "tightening" of the network. AFM results confirmed the microphase separated morphology and rough agreement was observed with the interdomain spacing obtained from the SAXS data.

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